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(11) **EP 0 259 974 B2**

(12) **NEW EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the opposition decision:  
**26.03.1997 Bulletin 1997/13**

(45) Mention of the grant of the patent:  
**12.05.1993 Bulletin 1993/19**

(21) Application number: **87307025.4**

(22) Date of filing: **07.08.1987**

(51) Int Cl.<sup>6</sup>: **C10M 159/22, C10M 159/24,**  
**C07C 319/02**  
**// C10N10/04, C10N20/02,**  
**C10N30/04, C10N30/12,**  
**C10N70/00**

(54) **Overbased sulfurized alkyl-phenols as lubricating oil additives**

Überbasisch gemachte, sulfurierte Alkylphenole und ihre Verwendung als Schmieröl-Additive  
Alkyl phénols soufrés surbasés et leur utilisation comme additifs pour des huiles lubrifiantes

(84) Designated Contracting States:  
**BE DE ES FR GB IT NL SE**

(30) Priority: **08.08.1986 US 894599**

(43) Date of publication of application:  
**16.03.1988 Bulletin 1988/11**

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## Description

This invention relates to a process for preparing Group II metal highly overbased sulfurized alkylphenols, lubricating oil compositions containing them and lubricating oil concentrates containing them.

Group II metal overbased sulfurized alkylphenols are useful lubricating oil additives which impart detergency and dispersancy properties to the lubricating oil composition as well as providing for an alkalinity reserve in the oil. Alkalinity reserve is necessary in order to neutralize acids generated during engine operation. Without this alkalinity reserve, the acids so generated would result in harmful engine corrosion.

US-3424679 and US-3464970 disclose overbased sulfurized phenates useful as detergents for lubricating oils.

One method of preparing Group II metal overbased sulfurized alkylphenols is described in U.S. Patent No. 3,178,368 where the alkylphenol, a sulfonate, a high molecular weight alcohol, lubricating oil and sulfur are combined and heated with agitation. Hydrated lime is then added, the system heated and ethylene glycol added. Water of reaction is removed, the mixture cooled, and carbon dioxide added. Uncombined CO<sub>2</sub> is removed and the vessel is heated to remove ethylene glycol, water and the high molecular weight alcohol. The product is overbased by the incorporation therein of hydrated lime and carbon dioxide.

Such prior art methods provide for Group II metal overbased sulfurized alkylphenols of approximately 250 TBN (Total Base Number). Greater than 275 TBN Group II metal overbased sulfurized alkylphenols of the prior art are too viscous and require inefficiently large amounts of diluent in order to be conveniently handled. See U.S. Patent No. 3,367,867. In order to overcome the problem of extremely high viscosities associated with high TBN Group II metal overbased sulfurized alkylphenols, U.S. Patent No. 3,367,867 discloses that the use of alkyl groups on the alkylphenol which are mixtures of straight and branched chain alkyl results in products having suitable viscosities as well as anti-foaming properties. Commercial products encompassed by U.S. Patent No. 3,367,867 are generally about 250 TBN.

While the process disclosed in U.S. Patent No. 3,367,867 is useful in preparing 250 TBN products of acceptable viscosity, attempts to extend this technology to prepare extremely high TBN Group II metal overbased sulfurized alkylphenols, about 300 TBN and greater, resulted in increased viscosity as well as increasing hydrolytic instability in the products. Accordingly, there is a need to develop extremely high TBN Group II metal overbased sulfurized alkylphenols of suitable viscosity. It would be an additional advantage if such high TBN Group II metal overbased sulfurized alkylphenols of suitable viscosity were also hydrolytically stable.

We have now discovered a process for preparing novel Group II metal overbased sulfurized alkylphenols characterized as possessing a Total Base Number of about 300 and greater and having viscosities of about 800 centistokes and less at 100°C. The novel products of this invention are also surprisingly hydrolytically stable.

The Group II metal overbased sulfurized alkylphenols are prepared by employing, inter alia, a suitable alkylphenol and a sulfur-containing "sulfurization catalyst" in the preparation of these additives. A particularly preferred catalyst is 2-mercapto-benzothiazole (MBT) and derivatives thereof.

To our knowledge, the use of a sulfur-containing sulfurization catalyst in the preparation of Group II metal overbased sulfurized alkylphenols is not taught in the prior art. Prior art references include U.S. Patent No. 3,923,670 which describes the use of a more than catalytic amount of alkali metal hydroxide to produce an overbased sulfurized alkylphenol containing a significant amount of alkali metal in the reaction product; and U.S. Patent No. 4,100,085 which describes the use of ammonia or ammonium hydroxide as a promoter in the synthesis of overbased sulfurized alkylphenols. Likewise, U.S. Patent No. 4,212,752 describes the use of certain amino promoters, such as primary and secondary alkylamines, polyalkyleneamines, amino acids, etc. in the synthesis of overbased sulfurized alkylphenols.

In accordance with a first aspect of the present invention, there is provided a process for preparing a lubricating oil additive comprising an oil-soluble hydrolytically stable Group II metal overbased sulfurized alkylphenol characterized as possessing a Total Base Number of at least 300 and a viscosity of not more than 800 centistokes at 100°C and containing less than 10 mole percent (in the actives) of unsulfurized Group II metal alkylphenol, which process comprises the following steps:

- (a) reacting, in a lubricating oil, an alkylphenol, sufficient sulfur to convert the alkylphenol to sulfurized alkylphenol, a catalytic amount of a sulfur-containing sulfurization catalyst and a Group II metal oxide, hydroxide or C<sub>1</sub>-C<sub>6</sub> alkoxide, the molar charge of the Group II metal oxide, hydroxide or C<sub>1</sub>-C<sub>6</sub> alkoxide to alkylphenol being greater than 2; and
- (b) carbonating the reaction product of step (a) with CO<sub>2</sub>

In accordance with another aspect of the present invention, there is provided, in the production of an oil-soluble, Group II metal overbased sulfurized alkylphenol by a process having the following steps:

- (a) reacting, in a lubricating oil, an alkylphenol, sufficient sulfur to convert the alkylphenol to sulfurized alkylphenol and a Group II metal oxide, hydroxide or C<sub>1</sub>-C<sub>6</sub> alkoxide, the molar charge of the Group II metal oxide, hydroxide

or C<sub>1</sub>-C<sub>6</sub> alkoxide to alkylphenol being greater than 2; and  
 (b) carbonating the reaction product of step (a) with CO<sub>2</sub>;

the use of a catalytic amount of a sulfur-containing sulfurization catalyst in step (a) for the purpose of obtaining a reaction product which has a Total Base Number of at least 300, a viscosity of not more than 800 centistokes at 100°C and less than 10 mole percent (in the actives) of unsulfurized Group II metal alkylphenol.

The present invention provides a process for preparing low viscosity, high TBN, Group II metal overbased sulfurized alkylphenols useful as lubricating oil additives having detergency and dispersancy properties.

The alkyl group of the alkylphenol contains a sufficient number of carbon atoms to render the Group II metal overbased sulfurized alkylphenol oil soluble. In one preferred embodiment, the alkyl group of said alkylphenol contains from 25 to 100 mole percent predominantly straight chain alkyl groups of from 15 to 35 carbon atoms and from 75 to 0 mole percent of the alkyl groups are polypropenyl of from 9 to 18 carbon atoms. More preferably, the alkyl group of said alkylphenol contains from 35 to 100 mole percent predominantly straight chain alkyl groups of from 15 to 35 carbon atoms and from 65 to 0 mole percent of the alkyl groups are polypropenyl of from 9 to 18 carbon atoms. In yet another preferred embodiment the alkyl group of said alkylphenol contains from 40 to 70 mole percent predominantly straight chain alkyl groups of from 15 to 35 carbon atoms and from 60 to 30 mole percent of the alkyl groups are polypropenyl of from 9 to 18 carbon atoms. Most preferably, the alkyl group of said alkylphenol contains approximately 50 mole percent predominantly straight chain alkyl groups of from 15 to 35 carbon atoms and approximately 50 mole percent of the alkyl groups are polypropenyl of from 9 to 18 carbon atoms.

Preferably, the Group II metal overbased sulfurized alkylphenols prepared in accordance with this invention possess a Total Base Number (TBN) of from about 300 to 400, more preferably from 315 to 400; even more preferably from 315 to 360; and most preferably from 325 to 360.

The oil-soluble, Group II metal overbased sulfurized alkylphenols prepared in accordance with this invention are useful lubricating oil additives imparting detergency and dispersancy properties to the lubricating oil as well as providing an alkalinity reserve in the oil. When employed in this manner, the amount of the oil-soluble, Group II metal overbased sulfurized alkylphenol ranges from about 0.5 to 40 weight percent of the total lubricant composition although preferably from about 1 to 25 weight percent of the total lubricant composition. Accordingly, another aspect of this invention is a lubricating oil composition comprising an oil of lubricating viscosity and from about 0.5 to 40 weight percent of an oil-soluble, Group II metal overbased sulfurized alkylphenol prepared in accordance with the first aspect of this invention. Lubricating oil compositions of this invention are useful in diesel engines, gasoline engines as well as in marine engines. When employed in marine engines, the oil-soluble, Group II metal overbased sulfurized alkylphenols are often used in conjunction with an oil-soluble Group II metal overbased natural or synthetic hydrocarbyl sulfonate. Therefore, still another aspect of this invention is a lubricating oil composition comprising an oil of lubricating viscosity and (a) from about 0.5 to 40 weight percent of an oil-soluble, Group II metal overbased sulfurized alkylphenol prepared in accordance with the first aspect of this invention; and (b) from about 0.5 to 40 weight percent of an oil-soluble Group II metal overbased natural or synthetic hydrocarbyl sulfonate.

As used herein, the term "Total Base Number" or "TBN" refers to the amount of base equivalent to milligrams of KOH in 1 gram of sample. Thus, higher TBN numbers reflect more alkaline products and therefore a greater alkalinity reserve.

The term "hydrolytically stable" as used in conjunction with Group II metal overbased sulfurized alkylphenols means that compositions containing these products will lose less than about 25% of their Total Base Number in a modified ASTM D 2619 test. This test, as modified, measures the hydrolytic stability of a product by measuring its base loss upon exposure to moisture. Greater base loss reflects poorer hydrolytic stability. Hydrolytic stability of the Group II metal overbased sulfurized alkylphenols is an extremely important property particularly in marine crankcase use where water exposure is common. See van der Horst, *Lubricant Engineering*, "Development of Modern Lubricants for Medium-Speed Marine Diesel Engines" (1977); Thomas et al., "Modern Marine Diesel Engine Lubricants and their Development", Second International Lubricant Symposium, Cairo, Egypt (1979).

In the process of preparing overbased sulfurized alkylphenols, only the Group II metal sulfurized alkylphenol is capable of being overbased. Accordingly, it is desirable to maximize the amount of Group II metal sulfurized alkylphenol in the reaction process. On the other hand, unsulfurized alkylphenol can form a Group II metal salt but this salt cannot be overbased by addition of Ca(OH)<sub>2</sub> (and related materials) and carbon dioxide. Accordingly, it is desirable to minimize the amount of Group II metal unsulfurized alkylphenol in the reaction process.

The term "actives" as applied to the compositions of this invention refers to the Group II metal alkylphenol and the Group II metal sulfurized alkylphenol whereas the term "inactives" refers to unreacted alkylphenol as well as any diluent oil contained in the composition.

The amount of Group II metal sulfurized alkylphenol as well as the amount of Group II metal alkylphenol contained in the actives can be determined by standard analytical techniques. One technique employed herein utilizes dialysis coupled with <sup>1</sup>H-NMR.

As used herein, the term "predominantly straight chain alkyl" means a predominantly linear alkyl group which may contain some branching in the molecular structure.

The Group II metal overbased sulfurized alkylphenols of this invention are prepared in processes similar to those previously described in the art with the exception that a sulfurization catalyst is also employed. Prior art processes for preparing Group II metal overbased sulfurized alkylphenols can provide products having a Total Base Number as high as 300 or more, some of which have acceptable viscosities but some of these products are hydrolytically unstable. The reasons for the inability of prior art processes to consistently produce hydrolytically stable high TBN overbased sulfurized alkylphenols is not readily apparent.

Upon careful examination of this problem and without limitation to this theory, it appears that the hydrolytic instability of high TBN products is due in part to large amounts of unsulfurized Group II metal alkylphenol contained in the actives. It appears that this incomplete sulfur incorporation is much more prevalent when high molar charges of hydrated lime to alkylphenol are used, i.e., greater than 2. That is to say, in the process of preparing an overbased sulfurized alkylphenol, hydrated lime, sulfur and alkylphenol are charged into a reaction system. Sufficient sulfur is employed to convert all of the alkylphenol to sulfurized alkylphenol. At a molar charge of 2 or less of hydrated lime to alkylphenol, the alkylphenol is generally converted to calcium sulfurized alkylphenol whereas at molar charges of greater than 2, the product contains large amounts of unsulfurized calcium alkylphenol. On the other hand, molar charges of hydrated lime to alkylphenol of greater than 2 are generally required to achieve 300 + TBN products. Thus, the problem is readily apparent. With all other factors held constant such as sulfur charge, CO<sub>2</sub> charge, etc., to arrive at 300+ TBN products requires molar charges of hydrated lime to alkylphenol in excess of 2 which invariably results in large amounts of unsulfurized calcium alkylphenol which in turn reduces the TBN incorporation because it cannot be overbased and tends to increase the viscosity of the product. The incomplete sulfurization of the alkylphenol at high molar charges of hydrated lime to alkylphenol, i.e., >2, was heretofore unrecognized and for which an explanation is not readily available.

In any event, we have now discovered that the use of a sulfurization catalyst in those processes employing greater than 2 equivalents of hydrated lime or other Group II metal oxide or hydroxide greatly enhances the amount of Group II metal sulfurized alkylphenol in the actives and greatly decreases the amount of unsulfurized Group II metal alkylphenol in the actives. The high TBN products of this invention are characterized by containing at least about 90 mole percent and preferably at least 95 mole percent of Group II metal sulfurized alkylphenols in the actives. In the converse, the products of this invention by necessity will contain at most about 10 mole percent and preferably at most about 5 mole percent of the unsulfurized Group II metal alkylphenols in the actives. Because of the decrease in the amount of unsulfurized Group II metal alkylphenol in the actives, the higher TBN products are possible. Moreover these products have improved hydrolytic stability as well as lower viscosity.

In accordance with this invention, it has been discovered that oil-soluble, Group II metal overbased sulfurized alkylphenols of this invention can be prepared by reacting in lubricating oil appropriate amounts of a sulfurization catalyst, sulfur, alkylphenol, a Group II metal oxide, hydroxide or C<sub>1</sub>-C<sub>6</sub> alkoxide followed by carbonation with CO<sub>2</sub>. The reaction system will also contain a C<sub>2</sub>-C<sub>4</sub> alkylene glycol (such as 1,3-propylene glycol, 1,4-butylen glycol, ethylene glycol, etc., but preferably the C<sub>2</sub>-C<sub>4</sub> alkylene glycol is ethylene glycol), a Group II metal overbased natural or synthetic hydrocarbyl sulfonate and a high molecular weight alcohol. The resulting products of this reaction are termed by the art as a Group II metal overbased sulfurized alkylphenols. The Group II metal overbased sulfurized alkylphenols of this invention are characterized by possessing a Total Base Number of about 300 or greater, a viscosity of about 800 centistokes or less at 100°C and containing about 10 mole percent or less of unsulfurized Group II metal alkylphenol.

The sulfurization catalyst catalyzes the sulfur incorporation onto the alkylphenol. Suitable sulfurization catalysts include 2-mercaptobenzothiazole (MBT) and derivatives thereof such as bis(2,2-benzothiazolyl) disulfide; 2(3H)-benzothiazolethione zinc salt; 2-benzothiazolyl-N,N'-diethylthiocarbamyl sulfide; 4-morpholinyl-2-benzothiazole disulfide; etc. Another suitable class of sulfurization catalysts include dithiophosphates such as zinc diisopropyl dithiophosphate; zinc di-n-butyl dithiophosphate) etc. Other suitable classes of sulfurization catalysts include thioureas, thiurams, calcium polysulfide and the like. Specific embodiments of these catalysts include N,N'-dibutylthiourea; ethylenethiourea; trimethylthiourea, dipentamethylenethiuram disulfide, dipentamethylenethiourea tetrasulfide; dipentamethylenethiourea hexasulfide; etc.

The sulfurization catalyst is generally employed at from about 0.5 to 10 weight percent to the alkylphenol in the reaction system and preferably at from about 1 to 2 weight percent. In a preferred embodiment, the sulfurization catalyst is added to the reaction mixture as a liquid. This can be accomplished by dissolving the sulfurization catalyst in molten sulfur or in the alkylphenol as a premix to the reaction.

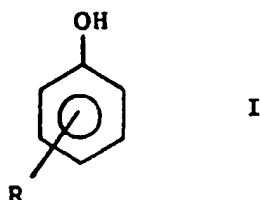
Sulfur is generally employed at from about 2 to 4 moles per mole of the alkylphenol in the reaction system and preferably at from about 2 to 3 moles per mole of alkylphenol. All allotropic forms of sulfur can be used. Alternatively, in place of sulfur, sulfur monochloride may be employed. For the purposes of this invention, sulfur monochloride is considered equivalent to sulfur. The sulfur may be employed either as molten sulfur or as a solid.

The Group II metal oxide, hydroxide or C<sub>1</sub>-C<sub>6</sub> alkoxide used to prepare the Group II metal alkylphenol includes

the oxides, hydroxides and alkoxides of calcium, strontium, barium or magnesium. However, calcium, barium and magnesium are preferred whereas calcium is most preferred. The Group II metal oxide, hydroxide, or C<sub>1</sub>-C<sub>6</sub> alkoxide is employed at a molar charge to the alkylphenol of from greater than 2 to 4; although more preferably from greater than 2 to 3.

Carbon dioxide is added to the reaction system in conjunction with the Group II metal oxide, hydroxide or C<sub>1</sub>-C<sub>6</sub> alkoxide to form overbased products and is generally employed from about 1 to 3 moles per mole of alkylphenol, although preferably from about 2 to 3 moles per mole of alkylphenol charged to the reaction system.

The alkylphenol employed in this invention is represented by the formula:

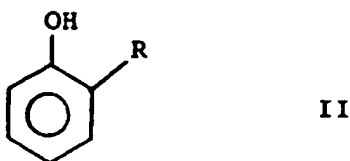


wherein R is an alkyl group containing sufficient number of carbon atoms to render the resulting Group II metal overbased sulfurized alkylphenol oil-soluble.

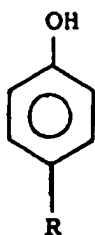
Preferably, R is alkyl wherein from about 25 to 100 mole percent of the alkyl group is predominantly straight chain alkyl of from 15 to 35 carbon atoms and from about 75 to 0 mole percent of the alkyl group is polypropenyl of from 9 to 18 carbon atoms although more preferably R is alkyl wherein from about 35 to 100 mole percent of the alkyl group is predominantly straight chain of from 15 to 35 carbon atoms and from about 65 to 0 mole percent of the alkyl group is polypropenyl of from 9 to 18 carbon atoms. Use of increasing amounts of predominantly straight chain alkyl results in high TBN products generally characterized by lower viscosities. On the other hand, while polypropenylphenols are generally more economical than predominantly straight chain alkylphenols, use of greater than 75 mole percent polypropenylphenol in the preparation of Group II metal overbased sulfurized alkylphenol generally results in products of unacceptably high viscosities. However, use of a mixture of from 75 mole percent or less of polypropenylphenol of from 9 to 18 carbon atoms and from 25 mole percent or more of predominantly straight chain alkylphenol of from 15 to 35 carbon atoms allows for more economical products of acceptable viscosities.

The alkylphenols of Formula I above are prepared by reacting the appropriate olefin or olefin mixture with phenol in the presence of an alkylating catalyst at a temperature of from about 60°C to 200°C, and preferably 125°C to 180°C either neat or in an essentially inert solvent at atmospheric pressure. A preferred alkylating catalyst is a sulfonic acid catalyst such as Amberlyst 15® available from Rohm and Haas, Philadelphia, Pennsylvania. Molar ratio of reactants may be used. Alternatively, molar excess of phenol can be employed, i.e., 2-2.5 equivalents of phenol for each equivalent of olefin with unreacted phenol recycled. The latter process maximizes monoalkylphenol. Examples of inert solvents include benzene, toluene, chlorobenzene and 250 thinner which is a mixture of aromatics, paraffins and naphthenes.

The alkylphenols employed in this invention are either ortho alkylphenols of the formula:

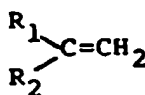


or para-alkylphenols of the formula:



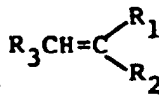
III

Preferably, R is predominantly para with no more than about 50 mole percent of the R alkyl group being in the ortho position; and more preferably no more than about 35 mole percent of the alkyl group being in the ortho position. It is believed that p-alkylphenols, III, facilitate the preparation of highly overbased Group II metal sulfurized alkylphenols. Accordingly, it is desirable to employ an olefin which results in maximum para alkylphenol content in the alkylphenol. In this regard, while polypropene generally adds in the para position, olefins containing no branching will add at both the ortho or para position. One method of enhancing the para content of the alkylphenol prepared from straight chain olefins is by use of a predominantly straight chain olefin fractions containing some branching in the molecular structure at the double bond such as structures IV and V



IV

(vinylidene)



V

(trisubstituted vinyl)

wherein  $R_1$ ,  $R_2$  and  $R_3$  form the remainder of the olefin. While being predominantly straight chain, the branched portion of the molecular structure allows for formation of a tertiary carbonium ion during the alkylation process. Without being limited to any theory, it is believed that the steric hindrance associated with a tertiary carbonium ion inhibits ortho alkylation and thereby results in enhanced para substitution. Suitable predominantly straight chain olefins are those wherein about 75 to 100 number percent and preferably about 85 to 100 number percent of the individual carbon atoms of the olefin are either primary ( $\text{CH}_3$ -) or secondary ( $-\text{CH}_2$ -). Included in the terms primary or secondary are alpha olefins ( $-\text{CH}=\text{CH}_2$ ) and internal olefins ( $-\text{CH}=\text{CH}-$ ). In the converse, such predominantly straight chain olefins can contain from 0 to about 25 number percent although preferably from 0 to about 15 number percent of tertiary carbon atoms. Included within the term tertiary are trisubstituted vinyl groups ( $>\text{C}=\text{CH}-$ ) and vinylidene ( $>\text{C}=\text{CH}_2$ ).

Predominantly straight chain olefin fractions are commercially available products such as  $\text{C}_{18}$ - $\text{C}_{30}$  olefins, available from Ethyl Corporation, Baton Rouge, Louisiana. These olefins are predominantly straight chain in that from 80 to 100 number percent of the carbon atoms in the olefins are either primary or secondary. On the other hand, about 40 mole percent of the olefins contained in the olefin fraction are branched olefins. That is to say while being otherwise predominantly straight chain 40 mole percent of all of the olefins are branched in the form of trisubstituted vinyl or vinylidene structure. Likewise,  $\text{C}_{24}$ - $\text{C}_{28}$  olefin fractions, available from Chevron Chemical Corporation, San Francisco, CA, are also predominantly straight-chain but contain about 40 mole percent or more branched olefin, containing predominantly vinylidene olefin. Straight chain olefins, containing less than about 5 mole percent branched olefins, are available from Shell Chemical Company, Houston, Texas.

This is the appropriate time to distinguish between "predominantly straight-chain olefins containing 80 to 100 number percent of either primary or secondary carbon atoms in the olefin" and a "predominantly straight-chain olefin fraction wherein about 40 mole percent of the olefins are branched". In the first case, the olefin is viewed on a molecular basis and requires that at least 80 number percent of the carbon atoms be primary or secondary. In this case, a branched olefin such as trisubstituted vinyl or vinylidene is nonetheless predominantly straight-chain if a sufficient number of the remaining carbon atoms are primary or secondary such that at least 80 number percent of the carbon atoms in this olefin are primary or secondary.

On the other hand, a predominantly straight-chain olefin fraction wherein about 40 mole percent of the olefins are branched as is viewed from a composition basis. That is the predominantly straight-chain olefin fraction can contain olefins such as alpha olefins, internal olefins, trisubstituted vinyl and vinylidene. When viewing the entire predominantly

straight-chain olefin fraction, 40 mole percent of the olefins are branched, i.e., either trisubstituted vinyl or vinylidene, whereas the remainder are either alpha olefins or internal olefins.

The reaction to prepare the Group II metal overbased sulfurized alkylphenols of this invention also employs an alkylene glycol, e.g., ethylene glycol, a high molecular weight alcohol (generally decyl alcohol) and a Group II metal overbased natural or synthetic hydrocarbyl sulfonate.

The ethylene glycol is generally employed at a molar charge to the alkylphenol of about 1 to 4, although preferably this molar charge is from about 2 to 3. Alternatively, 2-ethylhexanol may be employed in conjunction with ethylene glycol at weight ratios such as 80% by weight 2-ethylhexanol and 20% by weight ethylene glycol.

The preferred high molecular weight alcohol is decyl alcohol which is employed at a molar charge to the alkylphenol from about 0.5 to 4, although preferably from about 1 to 2.

The Group II metal overbased natural or synthetic hydrocarbyl sulfonates may be either petroleum sulfonate, synthetically alkylated aromatic sulfonates, or aliphatic sulfonates such as those derived from polyisobutylene. These sulfonates are well-known in the art. The hydrocarbyl group must have a sufficient number of carbon atoms to render the sulfonate molecule oil soluble. Preferably, the hydrocarbyl portion has at least 20 carbon atoms and may be aromatic or aliphatic, but is usually alkylaromatic. Most preferred for use are calcium, magnesium or barium sulfonates which are aromatic in character.

Certain sulfonates are typically prepared by sulfonating a petroleum fraction having aromatic groups, usually mono- or dialkylbenzene groups, and then forming the metal salt of the sulfonic acid material. Other feedstocks used for preparing these sulfonates include synthetically alkylated benzenes and aliphatic hydrocarbons prepared by polymerizing a mono- or diolefin, for example, a polyisobutenyl group prepared by polymerizing isobutene. The metallic salts are formed directly or by metathesis using well-known procedures.

The sulfonates are then overbased to yield products having Total Base Numbers up to about 400 or more by addition of carbon dioxide and a Group II metal hydroxide or oxide. Calcium hydroxide or oxide is the most commonly used material to produce the basic overbased sulfonates. These materials are well-known in the art.

The Group II metal overbased natural or synthetic hydrocarbyl sulfonate is employed at from about 1 to 20 weight percent to the alkylphenol, although preferably from about 1 to 10 weight percent. The Group II metal overbased natural or synthetic hydrocarbyl sulfonate described above are also employed in lubricating oil formulations in conjunction with the Group II metal overbased sulfurized alkylphenols; especially in marine crankcase formulations.

Alternatively, in lieu of a Group II metal overbased natural or synthetic hydrocarbyl sulfonate, an alkenyl succinimide may be employed. Alkenyl succinimides are well-known in the art. The alkenyl succinimides are the reaction product of a polyolefin polymer-substituted succinic anhydride with an amine, preferably a polyalkylene polyamine. The polyolefin polymer-substituted succinic anhydrides are obtained by reaction of a polyolefin polymer or a derivative thereof with maleic anhydride. The succinic anhydride thus obtained is reacted with the amine compound. The preparation of the alkenyl succinimides has been described many times in the art. See, for example, U.S. Patent Nos. 3,390,082; 3,219,666; and 3,172,892, the disclosure of which are incorporated herein by reference. Reduction of the alkenyl substituted succinic anhydride yields the corresponding alkyl derivative. The alkyl succinimides are intended to be included within the scope of the term "alkenyl succinimide". A product comprising predominantly mono- or bis-succinimide can be prepared by controlling the molar ratios of the reactants. Thus, for example, if one mole of amine is reacted with one mole of the alkenyl or alkyl substituted succinic anhydride, a predominantly mono-succinimide product will be prepared. If two moles of the succinic anhydride are reacted per mole of polyamine, a bis-succinimide will be prepared.

The polyisobutene from which the polyisobutene-substituted succinic anhydride is obtained by polymerizing isobutene can vary widely in its compositions. The average number of carbon atoms can range from 30 or less to 250 or more, with a resulting number average molecular weight of about 400 or less to 3,000 or more. Preferably, the average number of carbon atoms per polyisobutene molecule will range from about 50 to about 100 with the polyisobutenes having a number average molecular weight of about 600 to about 1,500. More preferably, the average number of carbon atoms are polyisobutene molecule ranges from about 60 to about 90, and the number average molecular weight ranges from about 800 to 1,300. The polyisobutene is reacted with maleic anhydride according to well-known procedures to yield the polyisobutene-substituted succinic anhydride.

In preparing the alkenyl succinimide, the substituted succinic anhydride is reacted with a polyalkylene polyamine to yield the corresponding succinimide. Each alkylene radical of the polyalkylene polyamine usually has up to about 8 carbon atoms. The number of alkylene radicals can range up to about 8. The alkylene radical is exemplified by ethylene, propylene, butylene, trimethylene, tetramethylene, pentamethylene, hexamethylene, octamethylene, etc. The number of amino groups generally, but not necessarily, is one greater than the number of alkylene radicals present in the amine, i.e., if a polyalkylene polyamine contains 3 alkylene radicals, it will usually contain 4 amino radicals. The number of amino radicals can range up to about 9. Preferably, the alkylene radical contains from about 2 to about 4 carbon atoms and all amine groups are primary or secondary. In this case, the number of amine groups exceeds the number of alkylene groups by 1. Preferably, the polyalkylene polyamine contains from 3 to 5 amine groups. Specific examples of

the polyalkylene polyamines include ethylenediamine, diethylenetriamine, triethylenetetramine, propylenediamine, tripropylenetetramine, tetraethylenepentamine, trimethylenediamine, pentaethylenhexamine, di-(trimethylene)tri-amine, tri(hexamethylene)tetramine, etc.

When employed the amount of alkenyl succinimide used is from about 1 to 20 weight percent to the alkylphenol, although preferably from about 1 to 10 weight percent.

The reaction to prepare the Group II metal overbased sulfurized alkylphenols of this invention is conducted by adding at the appropriate ratios the alkylphenol, the Group II metal overbased natural or synthetic hydrocarbyl sulfonate, the high molecular weight alcohol, and the sulfurization catalyst. The reaction is generally conducted in an inert diluent such as lubricating oil. Suitable lubricating oil diluent include solvent refined 100N, i.e., Cit Con 100N, and hydrotreated 100N, i.e. RLOP 100N. After combination of the above, the system is heated to between 90°C and 155°C with agitation and sulfur as well as the Group II metal oxide, hydroxide or C<sub>1</sub>-C<sub>6</sub> alkoxide is added followed by addition of the ethylene glycol. Water of reaction is removed, the mixture heated to about 175°C, and carbon dioxide added. Afterwards, any uncombined carbon dioxide is removed and the reaction system heated to remove ethylene glycol, water and the high molecular weight alcohol to yield a composition termed by the art as a Group II metal overbased sulfurized alkylphenol.

In a preferred embodiment, it has been found that the addition of a demulsifier such as Triton X-45 and Triton X-100 may synergistically enhance the hydrolytic stability of the Group II metal overbased sulfurized alkylphenol. Triton X-45 and Triton X-100 are nonionic detergents useful as demulsifiers and are available from Rohm and Haas, Philadelphia, PA. These demulsifiers are ethoxylated p-octylphenols. Other suitable demulsifiers include Igepal CO-610 available from GAF Corporation, New York, NY. In one preferred embodiment, the demulsifier and sulfurization catalyst is combined. That is the aqueous solution contains calcium polysulfide and Triton X-100. Such a product is sold by Chevron Chemical Company, San Francisco, CA, under the trade name of ORTHORIX®. Demulsifiers are generally added at from 0.1 to 1 weight percent to the alkylphenol, preferably at from 0.1 to 0.5 weight percent.

The lubricating oil compositions of this invention employ a finished lubricating oil which may be single or multigrade. Multigrade lubricating oils are prepared by adding viscosity index (VI) improvers. Typical viscosity index improvers are polyalkyl methacrylates, ethylene, propylene copolymers, styrene-diene copolymers and the like. So-called decorated VI improvers having both viscosity index and dispersant properties are also suitable for use in the formulations of this invention.

The lubricating oil used in the compositions of this invention may be mineral oil or synthetic oils of viscosity suitable for use in the crankcase of an internal combustion engine such as gasoline engines and diesel engines which include marine engines. Crankcase lubricating oils ordinarily have a viscosity of about 1300 cst 0°F to 24 cst at 210°F (99°C). The lubricating oils may be derived from synthetic or natural sources. Mineral oil for use as the base oil in this invention includes paraffinic, naphthenic and other oils that are ordinarily used in lubricating oil compositions. Synthetic oils include both hydrocarbon synthetic oils and synthetic esters. Useful synthetic hydrocarbon oils include liquid polymers of alpha-olefins having the proper viscosity. Especially useful are the hydrogenated liquid oligomers of C<sub>8</sub> to C<sub>12</sub> alpha-olefins such as 1-decene trimer. Likewise, alkyl benzenes of proper viscosity such as didodecyl benzene, can be used. Useful synthetic esters include the esters of both mono-carboxylic acid and polycarboxylic acids as well as mono-hydroxy alkanols and polyols. Typical examples are didodecyl adipate, pentaerythritol tetracaprate, di-2-ethylhexyl adipate, dilaurylsebacate and the like. Complex esters prepared from mixtures of mono and dicarboxylic acid and mono and dihydroxy alkanols can also be used.

Blends of hydrocarbon oils with synthetic oils are also useful. For example, blends of 10 to 25 weight percent hydrogenated 1-decene trimer with 75 to 90 weight percent 150 SUS (100°F) mineral oil gives an excellent lubricating oil base.

Lubricating oil additive concentrates are also included within the scope of this invention. The concentrate form comprises from about 60 to 20 weight percent of an oil of lubricating viscosity and from about 40 to 80 weight percent of an oil soluble, hydrolytically stable Group II metal overbased sulfurized alkylphenol of this invention.

Other additives which may be present in the formulation include rust inhibitors, foam inhibitors, corrosion inhibitors, metal deactivators, pour point depressants, antioxidants, and a variety of other wellknown additives.

The following examples are offered to specifically illustrate the invention. These examples and illustrations are not to be construed in any way as limiting the scope of the invention.

It is noted that two titrimeters were employed to measure the TBN of some of the examples herein. The TBN's reported herein were obtained from either titrimer. The TBN's obtained from these two titrimeters were within 3-5% of each other. It is understood that the TBN values reported herein are believed to be accurate at ±5%. TBN's obtained from both titrimeters are reported for some of the examples.



EXAMPLESExample 15 Preparation of a C<sub>18</sub>-C<sub>30</sub> Alkylphenol

To a 2-liter flask, equipped with stirrer, Dean Stark trap, condensor and nitrogen inlet and outlet was added 857  
 gms of a predominantly C<sub>18</sub> to C<sub>30</sub> olefin mixture (olefin content: C<sub>16</sub> -0.5%; C<sub>18</sub>-6.6; C<sub>20</sub>-26.2%; C<sub>22</sub>-27.7%; C<sub>24</sub>-  
 10 18.2%; C<sub>26</sub>-9.0%; C<sub>28</sub>-4.5%; C<sub>30</sub>-28%; greater than C<sub>30</sub>-4.5%) wherein in the entire olefin fraction, at least 30 mole  
 percent of said olefins contain trisubstituted vinyl groups (available from Ethyl Corporation, Baton Rouge, LA), 720  
 gms phenol, 55 gms of a sulfonic acid cation exchange resin (polystyrene crosslinked with divinylbenzene) catalyst  
 (Amberlyst 15® available from Rohm and Haas, Philadelphia, Pennsylvania). The reaction mixture was heated to about  
 145°C for about 6 hours with stirring under a nitrogen atmosphere. The reaction mixture was stripped by heating under  
 vacuum and the resulting product filtered hot over diatomaceous earth to afford 947 gms of a C<sub>18</sub>-C<sub>30</sub> alkylphenol with  
 15 a hydroxyl number of 118 and 56% para-alkylphenol content.

Example 220 Preparation of a C<sub>20</sub>-C<sub>28</sub> Alkylphenol

To a 2-liter flask, equipped with stirrer, Dean Stark trap, condensor and nitrogen inlet and outlet was added 674  
 gms of a predominantly C<sub>20</sub> to C<sub>28</sub> olefin mixture (olefin content: C<sub>18</sub>-2%; C<sub>20</sub>-28%; C<sub>22</sub>-19%; C<sub>24</sub>-13%; C<sub>26</sub>-21%; C<sub>28</sub>-  
 11%; and greater than C<sub>30</sub>-6%) wherein in the entire olefin fraction at least 20 mole percent of said olefins contain  
 vinylidene groups (C<sub>20</sub>-C<sub>24</sub> olefins and C<sub>24</sub>-C<sub>28</sub> olefins are available from Chevron Chemical Company, San Francisco,  
 25 CA and are then physically mixed at an equal mole basis to provide a C<sub>20</sub>-C<sub>28</sub> olefin mixture), 211.5 grams of phenol,  
 43 grams of a sulfonic acid cation exchange resin (polystyrene crosslinked with divinylbenzene) catalyst (Amberlyst  
 15® available from Rohm and Haas, Philadelphia, PA). The reaction mixture was heated to about 140 C for about 8  
 hours with stirring under a nitrogen atmosphere. The reaction mixture was stripped by heating under vacuum and the  
 product was filtered hot over diatomaceous earth to afford 574 grams of a C<sub>20</sub>-C<sub>28</sub> alkylphenol with a hydroxyl number  
 30 of 110 and with 56% para-alkylphenol content.

Example 335 Preparation of Tetrapropenylphenol

To a 2-liter flask, equipped with stirrer, Dean-Stark trap, condensor, and nitrogen inlet and outlet was added 567  
 grams of tetrapropylene, 540 grams of phenol, 72 grams of a sulfonic acid cation exchange resin (polystyrene  
 crosslinked with divinylbenzene) catalyst (Amberlyst 15® available from Rohm and Haas, Philadelphia, PA). The re-  
 action mixture was heated to about 110°C for about 3 hours with stirring under a nitrogen atmosphere. The reaction  
 40 mixture was stripped by heating under vacuum and the resulting product filtered hot over diatomaceous earth to afford  
 626 grams of tetrapropenylphenol and with a hydroxyl number of 205 and with 96% para-alkylphenol content.

Example 4

45 Into a 0.5-liter 3 neck-flask, equipped with stirrer, Dean-Stark trap, condensor, and nitrogen inlet and outlet was  
 charged 100 grams of phenol. The system was heated to 55°C and then charged with 55 grams of C<sub>24</sub>-C<sub>28</sub> olefin,  
 available from Chevron Chemical Company, San Francisco, CA, and 12.5 grams of Filtrol-13, an acid activated clay  
 available from Filtrol Corporation, Los Angeles, CA. Afterwards, 130.5 grams of C<sub>18</sub>-C<sub>30</sub> olefin, available from Ethyl  
 Corp., Baton Rouge, LA, was added over 1 hour while heating the system from between 135°C to 145°C. The reaction  
 50 was stopped and filtered. The filtered produce was transferred to a clean flask, placed under vacuum (-50 mm Hg) and  
 heated to 215°C with a small nitrogen sweep. The nitrogen was shut off and the vacuum (-50 mm Hg) continued at  
 215°C for 30 minutes to yield an alkylphenol having a hydroxyl number of 106.

55

Example 5Preparation of Calcium Overbased Hydrocarbyl Sulfonate5 A. Preparation of Sodium Hydrocarbyl Sulfonate

Into a reaction vessel is charged 646 grams of feedstock (solvent refined 500N lubricating oil which is a mixture of alkyl aromatics, naphthenes and paraffins). At 75°F, 150.8 grams of oleum (~27.6% SO<sub>3</sub>) is charged to the reaction vessel over a 10 minute addition period. The reaction temperature is allowed to rise - generally to about 100°F. After-  
 10 wards, 12.3 ml of water as well as 540 ml of Chevron 265 thinner, which is a mixture of aromatics, naphthenes and paraffins, is added to the system. The system is maintained at 150 F for 1 hour. At this time, 125 ml of an aqueous solution containing 25% by weight sodium hydroxide is added to the system. The reaction is maintained at 150°F for 1 hour. After settling, the aqueous layer is removed and the organic solution then is maintained for at least 1 hour. After this period, any additional aqueous layer which had settled out is also removed. The system is stripped at 350°F,  
 15 atmospheric pressure with an air sweep to yield the sodium hydrocarbyl sulfonate which is purified as follows: The sodium hydrocarbyl sulfonate is dissolved in 330 ml of aqueous secondary butyl alcohol. 160 ml of an aqueous solution containing 4% by weight sodium chloride is added to the system. The system is heated to 150°F and maintained at 150°F for 2 hours. After settling, brine is removed. An additional 80 ml of an aqueous solution containing 4% by weight sodium chloride is added to the system. The system is heated to 150°F and maintained at 150°F for 1 hour. After  
 20 settling, brine is removed. 220 ml of water is added to the system and the system heated to 150 F. The system is maintained at 150 F for 1 hour. Afterwards, water and unsulfonated oil layer is removed leaving the aqueous secondary butyl alcohol solution containing the sodium hydrocarbyl sulfonate.

25 B. Preparation of Calcium Hydrocarbyl Sulfonate

To the aqueous secondary butyl alcohol solution containing the sodium hydrocarbyl sulfonate, produced as in A above, is added 550 ml of a solution containing water, secondary butyl alcohol and calcium chloride (~10% CaCl<sub>2</sub>). The system is heated to 150°F and is maintained at 150°F for 1 hour. After settling, brine is removed. 340 ml of water and 170 ml of an aqueous solution containing 40% by weight calcium chloride is added to the system. The system is  
 30 heated to 150°F and is maintained at 150°F for at least 1 hour. After settling, brine is removed. 340 ml of water and 170 ml of an aqueous solution containing 40% by weight calcium chloride is added to the system. The system is heated to 150°F and is maintained at 150°F for at least 1 hour. After settling, brine is removed. 340 ml of water is added to the system. The system is heated to 150°F and is maintained at 150°F for 1 hour. After settling, the aqueous layer is removed. An additional 340 ml of water is then added to the system. The system is heated to 150°F and is maintained  
 35 at 150°F for 1 hour. After settling, the aqueous layer is removed. The aqueous secondary butyl alcohol solution is then stripped at elevated temperatures and reduced pressures to yield calcium hydrocarbyl sulfonate.

C. Preparation of Calcium Overbased Hydrocarbyl Sulfonate

40 Into a 500 ml 3-neck round bottom flask equipped with a mechanical stirrer, is added sufficient diluent oil to the calcium hydrocarbyl sulfonate, produced above, to yield 270 grams of a composition at 1.65% by weight calcium. 42.4 grams water and 10.8 grams calcium hydroxide are added to the system. A reflux condensor is attached to one side neck and a thermometer is attached to the other side neck of the 3-neck round bottom flask. The system is heated to reflux (~210°F) and held there for at least 1 hour. The reaction system is then distilled by heating to a bottoms tem-  
 45 perature of 330°F/atmospheric pressure. Afterwards, the temperature is raised to 400°F under vacuum (~20 mm Hg). The system is then cooled to 300°F and the vacuum is discontinued. 20 grams of diatomaceous earth is added to the product and the product filtered through a 1/4 inch diatomaceous earth pad on a Buchner funnel, which is preheated prior to filtration to yield the title compound which is generally of approximately 16 Total Base Number.

50 Example 6Preparation of 340 TBN Calcium Overbased Sulfurized Alkylphenol

55 Into a 2-liter, 4-neck flask was charged 196 grams of tetrapropenylphenol, prepared in a manner similar to Example 3, 354 grams of C<sub>18</sub>-C<sub>30</sub> alkylphenol, prepared in a manner similar to Example 1, 410 grams of decyl alcohol, 20 grams of 2-mercaptobenzothiazole, 40 grams of a calcium overbased hydrocarbyl sulfonate, prepared in a manner similar to Example 5 and 200 grams of Cit-Con 100N oil. The system was heated with agitation at 90°C at which time 296 grams of Ca(OH)<sub>2</sub> and 108 grams of sulfur were charged to the reaction system. The reaction system was then held at 90°C

for 45 minutes. Afterwards, the reaction temperature was raised over a 15 minute period to 150°C whereupon 206 grams ethylene glycol was added over a 60 minute period via an addition funnel. After complete addition of ethylene glycol, the reaction temperature was increased to 160°C over a 15 minute period and held at this temperature for 1 hour. At this time, the stirring rate of the reaction mixture was increased to moderately fast, and the reaction temperature was then increased at a rate of 5°C per 20 minutes until the reaction temperature reached 175°C whereupon 144 grams of carbon dioxide was charged through a flowmeter to the reaction system over a three hour period. The reaction temperature was then increased to 195°C and the system stripped under vacuum (~10 mm of Hg) for a period of 30 minutes to yield 1269 grams of product which was purified by addition of 3 weight percent diatomaceous earth consisting of 50% Hi-Flo, and 50% of 512 Celite, commercial diatomaceous earth products available from Manville, Filtration and Minerals Division, Denver, CO, followed by filtration through a 1/4 inch Celite pad on a Buchner funnel. The resulting product has a Total Base Number of 340 (324 on second titrimer); a viscosity of 720 centistokes at 100°C; a sulfur content of 4.4 weight percent; and a calcium content of 12.3 weight percent.

#### Example 7

##### Preparation of a 343 TBN Calcium Overbased Sulfurized Alkylphenol

Into a 10 gallon stainless steel reactor was charged 3.53 kilograms of tetrapropenylphenol, prepared in a manner similar to Example 3, 6.73 kilograms of C<sub>18</sub>-C<sub>30</sub> alkylphenol, prepared in a manner similar to Example 1, 7.6 kilograms of decyl alcohol, 380 grams of 2-mercaptobenzothiazole, 760 grams of a calcium overbased hydrocarbyl sulfonate, prepared in a manner similar to Example 5 and 3.8 kilograms of Cit-Con 100N oil. The system was heated with agitation to 90°C at which time 5.62 kilograms of Ca(OH)<sub>2</sub> and 2.05 kilograms sulfur were charged to the reaction system. The reaction system was then held at 90°C for 45 minutes. Afterwards, the reaction temperature was raised over a 15 minute period to 150°C whereupon 3.91 kilograms ethylene glycol was added over a 60 minute period via an addition flask. After complete addition of ethylene glycol, the reaction temperature was increased to 160°C and held at this temperature for 1 hour. At this time, the stirring rate of the reaction mixture was increased and the reaction temperature was then increased at a rate of 5°C per 20 minutes until the reaction temperature reached 175°C whereupon 2.74 kilograms of CO<sub>2</sub> was charged to the reaction system over a three hour period. The reaction temperature was then increased to 195°C and the system stripped under vacuum (~10 mm of Hg) for a period of 30 minutes. The system was cooled overnight and then heated and agitated. The product was then purified by addition of 3 weight percent diatomaceous earth consisting of 50% Hi-Flo, and 50% of 512 Celite, commercial diatomaceous earth products available from Manville, Filtration and Minerals Division, Denver, CO, followed by filtration to yield a product having a Total Base Number of 343 (324 on second titrimer); a viscosity of 463 centistokes at 100°C; a sulfur content of 4.4 weight percent, a calcium content of 12.4 weight percent and 1.6% crude sediment.

#### Example 8

Into a 1-liter, 4-neck flask was added 99 grams of tetrapropenylphenol, prepared in a manner similar to Example 3, 167 grams of a C<sub>20</sub>-C<sub>28</sub> alkylphenol, prepared in a manner similar to Example 2, 210 grams of decyl alcohol, 10 grams of 2-mercaptobenzothiazole, 20 grams of a calcium overbased hydrocarbyl sulfonate, prepared in a manner similar to Example 5 and 100 grams of Cit-Con 100N oil. The system was heated with agitation to 90°C at which time 148 grams of Ca(OH)<sub>2</sub> and 56 grams of sublimed sulfur were charged to the reaction system. The reaction was then held at 90°C for 45 minutes. Afterwards, the reaction temperature was raised over a 15 minute period to 150°C whereupon 103 grams of ethylene glycol was added over a 60 minute period. After complete addition of the ethylene glycol, the reaction temperature was increased to 160°C and held at this temperature for 1 hour. At this time, the reaction temperature was increased at a rate of 5°C per 20 minutes until the reaction temperature reached 175°C whereupon 72 grams of carbon dioxide was charged to the reaction system over a three hour period. The reaction temperature was then increased to 195°C and the system stripped under vacuum (~10 mm of Hg) for a period of 30 minutes. Sediment was removed and 800 ml of 250 thinner which is a mixture of aromatics, paraffins and naphthenes was added to the system as well as 3 weight percent diatomaceous earth consisting of 50% Hi-Flo and 50% of 512 Celite, commercial diatomaceous earth products available from Manville, Filtration and Minerals Division, Denver, CO. The system was filtered through a 1/4 inch Celite pad on a Buchner funnel. Afterwards, the thinner was removed by stripping at elevated temperatures and reduced pressures to yield 581 grams of a calcium overbased sulfurized alkylphenol having a Total Base Number of 328 (obtained from second titrimer) a viscosity of 365 centistokes at 100°C; a sulfur content of 3.96 weight percent; and a calcium content of 12.3 weight percent.

Example 9

Into a 1-liter, 4-neck flask was added 99 grams of tetrapropenylphenol, prepared in a manner similar to Example 3, 167 grams of a C<sub>20</sub>-C<sub>28</sub> alkylphenol, prepared in a manner similar to Example 2, 210 grams of decyl alcohol, 10 grams of ORTHORIX® a commercially available calcium polysulfide product sold by Chevron Chemical Company, San Francisco, CA, 20 grams of a calcium overbased hydrocarbyl sulfonate, prepared in a manner similar to Example 5 and 100 grams of Cit-Con 100N oil. The system was heated with agitation to 90°C at which time 148 grams of Ca(OH)<sub>2</sub> and 56 grams of sublimed sulfur were charged to the reaction system. The reaction was then held at 90°C for 45 minutes. Afterwards, the reaction temperature was raised over a 15 minute period to 150°C whereupon 103 grams of ethylene glycol was added over a 60 minute period. After complete addition of the ethylene glycol, the reaction temperature was increased to 160°C and held at this temperature for 1 hour. At this time, the reaction temperature was increased at a rate of 5°C per 20 minutes until the reaction temperature reached 175°C whereupon 72 grams of carbon dioxide was charged to the reaction system over a three hour period. The reaction temperature was then increased to 195°C and the system stripped under vacuum (~10 mm of Hg) for a period of 30 minutes. Sediment was removed and 800 ml of 250 thinner which is a mixture of aromatics, paraffins and naphthenes was added to the system as well as 3 weight percent diatomaceous earth consisting of 50% Hi-Flo, a commercial diatomaceous earth product available from Manville, Filtration and Minerals Division, Denver, CO, and 50% of 512 Celite, a commercial diatomaceous earth product available from Manville, Filtration and Minerals Division, Denver CO. The system was filtered through a 1/4 inch Celite pad on a Buchner funnel. Afterwards, the thinner was removed by stripping at elevated temperatures and reduced pressures to yield 500 grams of a calcium overbased sulfurized alkylphenol having a Total Base Number of 344 (obtained from second titrimeter); a viscosity of 632 centistokes at 100°C; a sulfur content of 3.31 weight percent; and a calcium content of 12.8 weight percent.

Example 10

Into a 2-liter, 4 neck flask was added 99 grams of tetrapropenylphenol, prepared in a manner similar to Example 3, 167 grams of a C<sub>20</sub>-C<sub>28</sub> alkylphenol, prepared in a manner similar to Example 2, 210 grams of decyl alcohol, 10 grams of 2-mercaptobenzothiazole, 20 grams of calcium overbased hydrocarbyl sulfonate, prepared in a manner similar to Example 5 and 100 grams of Cit-Con 100N oil. The system was heated with agitation to 90°C at which time 138 grams of calcined Dolomite, Ca(OH)<sub>2</sub>.Mg(OH)<sub>2</sub>, and 56 grams of sublimed sulfur were charged to the reaction system. The reaction was then held at 90°C for 45 minutes. Afterwards, the reaction temperature was raised over a 15 minute period to 150°C whereupon 103 grams of ethylene glycol was added over a 60 minute period. After complete addition of the ethylene glycol, the reaction temperature was increased to 160°C and held at this temperature for 1 hour. At this time, the reaction temperature was increased at a rate of 5°C per 20 minutes until the reaction temperature reached 175°C whereupon 74 grams of carbon dioxide was charged to the reaction system over a three hour period. The reaction temperature was then raised to 195°C and the system stripped under vacuum (~10 mm Hg) for a period of 30 minutes. Sediment was removed and 800 ml of Chevron 250 thinner, which is a mixture of aromatics, paraffins and naphthenes was added to the system as well as 3 weight percent diatomaceous earth consisting of 50% Hi-Flo and 50% 512 Celite, which are commercial diatomaceous earth products available from Manville, Filtration and Minerals Division, Denver, CO. The system was filtered through a 1/4 inch Celite pad on a Buchner funnel. Afterwards, the thinner was removed by stripping at elevated temperatures and reduced pressures to yield 280 grams of a calcium-magnesium overbased sulfurized alkylphenol having a Total Base Number of 294 (obtained from second titrimeter); a viscosity of 154 centistokes at 100°C; a sulfur content of 3.65 weight percent; a calcium content of 7.62 weight percent; and a magnesium content of 2.14 weight percent.

Example 11

Into a 1-liter, 3-neck flask was added 104 grams of tetrapropenylphenol, prepared in a manner similar to Example 3, 187 grams of a mixture of C<sub>18</sub>-C<sub>30</sub> and C<sub>24</sub>-C<sub>28</sub> alkylphenol, prepared in a manner similar to Example 4, 105 grams of decyl alcohol, 10 grams of 2-mercaptobenzothiazole, 20 grams of calcium overbased hydrocarbyl sulfonate, prepared in a manner similar to Example 5, and 100 grams of Cit-Con 100N oil. The system was heated with agitation to 90°C at which time 148 grams of Ca(OH)<sub>2</sub> and 56 grams of sublimed sulfur were charged to the reaction system. The reaction was then held at 90°C for 45 minutes. Afterwards, the reaction temperature was raised over a 15 minute period to 150°C whereupon 103 grams of ethylene glycol was added over a 60 minute period. After complete addition of the ethylene glycol, the reaction temperature was increased to 160°C and held at this temperature for 1 hour. At this time, the reaction temperature was increased at a rate of 5°C per 20 minutes until the reaction temperature reached 175°C whereupon 72 grams of carbon dioxide was charged to the reaction system over a three hour period. The reaction temperature was then raised to 195°C and the system stripped under vacuum (~10 mm Hg) for a period of 30 minutes.

Sediment was removed and 800 ml of Chevron 250 thinner, which is a mixture of aromatics, paraffins and naphthenes, was added to the system as well as 3 weight percent diatomaceous earth consisting of 50% of Hi-Flo and 50% 512 Celite, which are commercial diatomaceous earth products available from Manville, Filtration and Minerals Division, Denver, CO. The system was filtered through a 1/4 inch Celite pad on a Buchner funnel. Afterwards, the thinner was removed by stripping at elevated temperatures and reduced pressures to yield 601 grams of a calcium overbased sulfurized alkylphenol having a Total Base Number of 349 (324 TBN on second titrimeter), a viscosity of 441 centistokes at 100°C; a sulfur content of 4.27 weight percent; and a calcium content of 12.4 weight percent.

#### Example 12

Into a 1-liter, 3 neck flask was added 102 grams of tetrapropenylphenol, prepared in a manner similar to Example 3, 187 grams of a mixture of C<sub>18</sub>-C<sub>30</sub> and C<sub>24</sub>-C<sub>28</sub> alkylphenol, prepared in a manner similar to Example 4, 105 grams of decyl alcohol, 20 grams of 2-mercaptobenzothiazole, 20 grams of a polyisobutenyl succinimide dispersant composition [prepared by reacting 1 mole of polyisobutenyl succinic anhydride, where the polyisobutenyl group has a number average molecular weight of about 950, with 0.87 mole of tetraethylenepentaamine; then diluting to about 50% actives with diluent oil-contains 2.1% nitrogen] and 100 grams of Cit-Con 100N oil. The system was heated with agitation to 90°C at which time 148 grams of Ca(OH)<sub>2</sub> and 56 grams of sublimed sulfur were charged to the reaction system. The reaction was then held at 90°C for 45 minutes. Afterwards, the reaction temperature was raised over a 15 minute period to 150°C whereupon 103 grams of ethylene glycol was added over a 60 minute period. After complete addition of the ethylene glycol, the reaction temperature was increased to 160°C and held at this temperature for 1 hour. At this time, the reaction temperature was increased at a rate of 5°C per 20 minutes until the reaction temperature reached 175°C whereupon 72 grams of carbon dioxide was charged to the reaction system over a three hour period. The reaction temperature was then raised to 195°C and the system stripped under vacuum (~10 mm Hg) for a period of 30 minutes. Sediment was removed and 800 ml of Chevron 250 thinner which is a mixture of aromatics, paraffins and naphthenes, was added to the system as well as 3 weight percent diatomaceous earth consisting of 50% of Hi-Flo and 50% Celite, which are commercial diatomaceous earth products available from Manville, Filtration and Minerals Division, Denver, CO. The system was filtered through a 1/4 inch Celite pad on a Buchner funnel. Afterwards, the thinner was removed by stripping at elevated temperatures and reduced pressures to yield a calcium overbased sulfurized alkylphenol having a Total Base Number of 352 (obtained from first titrimeter); a viscosity of 893 centistokes at 100°C; a sulfur content of 4.02 weight percent; and a calcium content of 11.3 weight percent.

#### Example 13

In a mixer containing a hatch, a vent line, an overhead system connected to a vacuum line (jet), and a hotwell line, first vent the mixer overhead into the hotwell. Close the vapor line valve and then purge the mixer with a slight nitrogen draft. With heat sources turned off, add 357 gallons of a tetrapropenylphenol, prepared similarly to Example 3 above, heated at 180°F, and add 318 gallons of Cit-Con 100N oil, heated at 70°F. Add 630 gallons of a C<sub>20</sub>-C<sub>28</sub> alkylphenol, prepared similarly to Example 2 above, heated at 150°F; 70 gallons of a calcium overbased hydrocarbyl sulfonate, prepared similarly to Example 5 above, heated at 200°F; and 866 gallons of decyl alcohol heated at 70°F.

Start agitation and then adjust the mixer's temperature to 150°F. After shutting off the nitrogen, open the hatch and charge 275 lbs of 2-mercaptobenzothiazole to the system and after closing the hatch, heat the system at 200°F for 4 hours.

After insuring that the mixer is venting through the mixer to hotwell line, cool the system to 175°F. While agitating the system, add 4,010 lbs of hydrated lime. Open the vapor line to vent through the condensor, water receiver, to jets. Close the mixer-to-hotwell line, and adjust to 10 inches of Hg. vacuum. Heat to 260°F. Add 1,327 lbs sulfur, heated at 250°F. Heat to 300°F over a period of 1 hour. At which time, add 274 gallons of ethylene glycol over a 60 minute period. The ethylene glycol addition is started very slowly and after complete addition of the ethylene glycol, heat the system to 335°F over a period of 1 hour. Charge 1,680 lbs of carbon dioxide over 2 hours and 48 minutes. Upon carbon dioxide addition, allow the temperature to rise to 350°F.

After complete carbon dioxide addition, apply full vacuum-at least 28 inches of Hg. Heat to 400°F. Hold at these conditions for 30 minutes starting once 395°F is reached. Thereupon cool to 350°F and break vacuum with nitrogen adjusting to 5 psig to yield a calcium overbased sulfurized alkylphenol having a Total Base Number of 327 having a viscosity of 1375 centistokes at 100°C and containing 12.3% calcium, 3.70% sulfur and 0.8% crude sediment. Filter through diatomaceous earth and dilute with 5 weight percent 130N oil to yield a calcium overbased sulfurized alkylphenol having a TBN of 312, a viscosity of 660 centistokes at 100°C and containing 11.6% calcium, 3.32% sulfur and 0.02% sediment.

Comparative Example A(Compared to Examples 8 and 9)

5 Into a 1-liter, 4-neck flask was added 99 grams of tetrapropenylphenol, prepared in a manner similar to Example 3, 167 grams of a C<sub>20</sub>-C<sub>28</sub> alkylphenol, prepared in a manner similar to Example 2, 210 grams of decyl alcohol, 20 grams of a calcium overbased hydrocarbyl sulfonate, prepared in a manner similar to Example 5 and 100 grams of Cit-Con 100N oil. The system was heated with agitation to 90°C at which time 148 grams of Ca(OH)<sub>2</sub> and 56 grams of sublimed sulfur were charged to the reaction system. The reaction was then held at 90°C for 45 minutes. Afterwards, 10 the reaction temperature was raised over a 15 minute period to 150°C whereupon 103 grams of ethylene glycol was added over a 60 minute period. After complete addition of the ethylene glycol, the reaction temperature was increased to 160°C and held at this temperature for 1 hour. At this time, the reaction temperature was increased at a rate of 5°C per 20 minutes until the reaction temperature reached 175°C whereupon 72 grams of carbon dioxide was charged to the reaction system over a three hour period. The reaction temperature was then increased to 195°C and the system 15 stripped under vacuum (~10 mm of Hg) for a period of 30 minutes. Sediment was removed and 800 ml of 250 thinner which is a mixture of aromatics, paraffins and naphthenes was added to the system as well as 3 weight percent diatomaceous earth consisting of 50% Hi-Flo, a commercial diatomaceous earth product available from Manville, Filtration and Minerals Division, Denver, CO, and 50% of 512 Celite, a commercial diatomaceous earth product available from Manville, Filtration and Minerals Division, Denver, CO. The system was filtered through a 1/4 inch Celite pad on a 20 Buchner funnel. Afterwards, the thinner was removed by stripping at elevated temperatures and reduced pressures to yield 377 grams of a calcium overbased sulfurized alkylphenol having a Total Base Number of 296; a viscosity of 667 centistokes at 100°C; a sulfur content of 3.28 weight percent (average of 2 runs); and a calcium content of 11.6 weight percent.

25 Comparative Example B(Compared to Example 11)

30 Into a 1-liter, 3-neck flask was added 102 grams of tetrapropenylphenol, prepared in a manner similar to Example 3, 187 grams of a mixture of C<sub>18</sub>-C<sub>30</sub> and C<sub>24</sub>-C<sub>28</sub> alkylphenol prepared in a manner similar to Example 4, 105 grams of decyl alcohol, 20 grams of calcium overbased hydrocarbyl sulfonate, prepared in a manner similar to Example 5 and 100 grams of Cit-Con 100N oil. The system was heated with agitation to 90°C at which time 148 grams of hydrated lime, Ca(OH)<sub>2</sub>, and 56 grams of sublimed sulfur were charged to the reaction system. The reaction was then held at 90°C for 45 minutes. Afterwards, the reaction temperature was raised over a 15 minute period to 150°C whereupon 103 grams of ethylene glycol was added over a 60 minute period. After complete addition of the ethylene glycol, the reaction temperature was increased to 160°C and held at this temperature for 1 hour. At this time, the reaction temperature was increased at a rate of 5°C per 20 minutes until the reaction temperature reached 175°C whereupon 72 grams of carbon dioxide was charged to the reaction system over a three hour period. The reaction temperature was then raised to 195°C and the system stripped under vacuum (~10 mm Hg) for a period of 30 minutes. Sediment was 40 removed and 800 ml of Chevron 250 thinner, which is a mixture of aromatics, paraffins and naphthenes, was added to the system as well as 3 weight percent diatomaceous earth consisting of 50% Hi-flo and 50% 512 Celite, which are commercial diatomaceous earth products available from Manville, Filtration and Minerals Division, Denver, CO. The system was filtered through a 1/4 inch Celite pad on a Buchner funnel. Afterwards, the thinner was removed by stripping at elevated temperatures and reduced pressures to yield 525 grams of a calcium overbased sulfurized alkylphenol 45 having a Total Base Number of 329 (327 on a second titrimer), a viscosity of 1190 centistokes at 100°C; a sulfur content of 3.75 weight percent; a calcium content of 12.2 weight percent and a crude sediment of 5.2 weight percent.

Comparative Example C50 (Compared to Example 12)

Into a 1-liter, 3 neck flask was added 102 grams of tetrapropenylphenol, prepared in a manner similar to Example 3, 187 grams of a mixture of C<sub>18</sub>-C<sub>30</sub> and C<sub>24</sub>-C<sub>28</sub> alkylphenol, prepared in a manner similar to Example 4, 105 grams of decyl alcohol, 20 grams of a polyisobutenyl succinimide dispersant composition [prepared by reacting 1 mole of 55 polyisobutenyl succinic anhydride, where the polyisobutenyl group has a number average molecular weight of about 950, with 0.87 mole of tetraethylene pentaamine; then diluting to about 50% actives in diluent oil-contains 2.1% nitrogen] and 100 grams of Cit-Con 100N oil. The system was heated with agitation to 90°C at which time 148 grams of hydrated lime, Ca(OH)<sub>2</sub>, and 56 grams of sublimed sulfur were charged to the reaction system. The reaction was then held at

90°C for 45 minutes. Afterwards, the reaction temperature was raised over a 15 minute period to 150°C whereupon 103 grams of ethylene glycol was added over a 60 minute period. After complete addition of the ethylene glycol, the reaction temperature was increased to 160°C and held at this temperature for 1 hour. At this time, the reaction temperature was increased at a rate of 5°C per 20 minutes until the reaction temperature reached 175°C whereupon 72 grams of carbon dioxide was charged to the reaction system over a three hour period. The reaction temperature was then raised to 195°C and the system stripped under vacuum (~10 mm Hg) for a period of 30 minutes. Sediment was removed and 800 ml of Chevron 250 thinner, which is a mixture of aromatics, paraffins and naphthenes, was added to the system as well as 3 weight percent diatomaceous earth consisting of 50% Hi-Flo and 50% 512 Celite, which are commercial diatomaceous earth products available from Manville, Filtration and Minerals Division, Denver, CO. The system was filtered through a 1/4 inch Celite pad on a Buchner funnel. Afterwards, the thinner was removed by stripping at elevated temperatures and reduced pressures to yield a calcium overbased sulfurized alkylphenol having a Total Base Number of 331 (on first titrimeter), a viscosity of 907 centistokes at 100°C; a sulfur content of 3.94 weight percent; and a calcium content of 10.3 weight percent.

#### Comparative Example D

(Compared to Example 6)

Into a 2-liter, 4-neck flask was charged 104 grams of tetrapropenylphenol, prepared in a manner similar to Example 3, 178 grams of C18 -C30 alkylphenol, prepared in a manner similar to Example 1, 105 grams of decyl alcohol, 20 grams of a calcium overbased hydrocarbyl sulfonate, prepared in a manner similar to Example 5 and 100 grams of Cit-Con 100N oil. The system was heated with agitation at 90°C at which time 148 grams of Ca(OH)<sub>2</sub> and 56 grams of sublimed sulfur were charged to the reaction system. The reaction system was then held at 90°C for 45 minutes. Afterwards, the reaction temperature was raised over a 15 minute period to 150°C whereupon 103 grams of ethylene glycol was added over a 60 minute period via an addition funnel. After complete addition of ethylene glycol, the reaction temperature was increased to 160°C over a 15 minute period and held at this temperature for 1 hour. At this time, the stirring rate of the reaction mixture was increased to moderately fast, and the reaction temperature was then increased at a rate of 5°C per 20 minutes until the reaction temperature reached 175°C whereupon 72 grams of carbon dioxide was charged through a flowmeter to the reaction system over a three hour period. The reaction temperature was then increased to 195°C and the system stripped under vacuum (~10 mm Hg) for a period of 30 minutes to yield 608 grams of product which was purified by addition of 3 weight percent of diatomaceous earth consisting of 50% Hi-Flo and 50% Celite 512, commercial diatomaceous earth products available from Manville, Filtration and Minerals Division, Denver, CO, followed by filtration through a 1/4 inch Celite pad on a Buchner funnel. The resulting product has a total base number of 336 (335 TBN on second titrimeter); a viscosity of 1323 centistokes at 100°C; a sulfur content of 3.95%; and a calcium content of 12.5%.

Table I below illustrates the side-by-side comparison of some of the Examples with the Comparative Examples.

TABLE I

	Catalyst	TBN	Viscosity (100°C)	Weight % Sulfur	Weight % Calcium	Crude Sediment
Example 8	MBT	328 <sup>B</sup>	365 Centistokes	3.96	12.3	1.2%
Example 9	ORTHORIX®	344 <sup>B</sup>	632 Centistokes	3.31	12.8	4%
Comparative Example A	None	296 <sup>B</sup>	667 Centistokes	3.28	11.6	7.2%
Example 11	MBT	349 <sup>A</sup>	441 Centistokes	4.27	12.4	2.8%
Comparative Example B	None	329 <sup>A</sup>	1190 Centistokes	3.75	12.2	5.2%
Example 12	MBT	352 <sup>A</sup>	893 Centistokes	4.02	11.3	2.8%

A - TBN value from the first titrimeter

B - TBN value from the second titrimeter

TABLE I (continued)

	Catalyst	TBN	Viscosity (100°C)	Weight % Sulfur	Weight % Calcium	Crude Sediment
5	Comparative Example C	None	331 <sup>A</sup> 907 Centistokes	3.94	10.3	3.2%
	Example 6	MBT	340 <sup>B</sup> 720 Centistokes	4.4	12.3	1.4%
10	Comparative Example D	None	336 <sup>B</sup> 1323 Centistokes	3.95	12.5	2.4%

A - TBN value from the first titrimeter

B - TBN value from the second titrimeter

15 Table I demonstrates that, under similar conditions, use of a sulfurization catalyst generally results in a higher TBN product of lower viscosity, and with lower crude sediment than is available without use of a sulfurization catalyst.

In Tables II and III below, Examples 14-17 further illustrate high TBN, low viscosity products of this invention. These products were prepared similarly to Examples 6-13 above.

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TABLE II

Ex.*	AP	lime/AP mole ratio	sulfur/AP mole ratio	Catalyst	grams of catalyst	CO <sub>2</sub> /AP mole ratio	grams of decyl alcohol	ethylene glycol/AP mole ratio
14	A	2.7	2.07	MBT	10	2.21	210	2.01
15	A	2.7	2.36	MORFAX <sup>1</sup>	10	2.21	210	2.24
16	A	2.7	2.36	ORTHORIX <sup>2</sup>	10	2.21	210	2.24
17	B	2.7	2.36	MBT	10	2.21	105	2.24

\*Examples 14-17 were all conducted employing 20 grams of a calcium overbased hydrocarbyl sulfonate and 100 grams of Cit-Con 100N oil

AP = alkylphenol

A = 0.74 mole of total alkylphenol (0.37 mole tetrapropenylphenol and 0.37 mole - C<sub>20</sub>-C<sub>28</sub> alkylphenol)

B = 0.74 mole of total alkylphenol (0.37 mole tetrapropenylphenol and 0.37 mole - C<sub>18</sub>-C<sub>30</sub>+ alkylphenol)

1. Morfax = a commercial formulation of R. T. Vanderbilt Co., Norwalk, CT, which contains 2-(4-morpholinylidithio)benzothiazole

2. ORTHORIX<sup>2</sup> - a commercial formulation of Chevron Chemical Company, San Francisco, CA, which contains 25% by weight calcium polysulfide, 65% by weight water, 10% by weight of Triton X-45 - a commercially available demulsifier available from Rohm and Haas, Philadelphia, PA and a foam inhibitor

TABLE III

	TBN	Viscosity (100°C)	Weight % Sulfur	Weight % Calcium	Crude Sediment
Ex. 14 <sup>C</sup>	338	561±28	4.3	12.2	2.8
Ex. 15	324	360	3.74	12.4	2.0
Ex. 16	337	501	3.49	12.7	2.0
Ex. 17	331	424	4.1	12.7	1.6

C - after a 3% dilution with Cit-Con 100N.

The Group II metal overbased sulfurized alkylphenols of this invention are characterized by containing at least about 90% and preferably at least 95% of Group II metal sulfurized alkylphenols in the actives and no more than about 10% and preferably no more than about 5% of Group II metal unsulfurized alkylphenols in the actives. Prior art Group II metal overbased sulfurized alkylphenols of 300 + TBN contain significantly more than 10% of Group II metal unsulfurized alkylphenol in the actives. Prior art compositions can be prepared either by a one step process as in Comparative Examples A-D above or in a two step process as shown in Comparative Example E below.

#### Comparative Example E

##### STEP 1 - Formation of Sulfurized Alkylphenol Calcium Salt

Into a 3-liter, 3-neck flask was added 529 grams of tetrapropenylphenol, prepared in a manner similar to Example 3. 274 grams of a C<sub>18</sub>-C<sub>30</sub> alkylphenol, prepared in a manner similar to Example 1, 250 grams of Cit - Con 100N. The system was heated to 90°C and 50 grams of Ca(OH)<sub>2</sub> and 112.5 grams of sublimed sulfur were added. The system was heated to 175°C and 32.5 grams of ethylene glycol was added over thirty minutes. The system was held at 175°C for one hour and then vacuum (~10 mm Hg) was applied for four hours to strip the ethylene glycol. 127.5 grams of C<sub>15</sub>-C<sub>18</sub> alpha olefin derived from cracked wax was added at 135°C along with 122.5 grams of Cit-Con 100N and the system heated for 8 hours under nitrogen. The product was filtered through a 50-50 mixture of Hi-Flo and Celite 512, diatomaceous earth products available from Manville, Filtration and Minerals Division, Denver, CO, to give 1351 grams of product with a Total Base Number of 63 containing 1.94 weight percent of calcium and 4.47 weight percent of sulfur.

##### STEP 2 - Formation of Overbased Sulfurized Alkylphenol Calcium Salt

Into a 1 - liter, 3 - neck flask was added 380 grams of the product prepared in Step 1, 20 grams of a polyisobutenyl succinimide dispersant composition [prepared by reacting 1 mole of polyisobutenyl succinic anhydride, where the polyisobutenyl group has a number average molecular weight of 950, with 0.87 mole of tetraethylene pentaamine, then diluting to about 50% actives with diluent oil], 48 grams of decyl alcohol and the system was heated to 90°C; 106 grams of Ca(OH)<sub>2</sub> was added while the system was heated to 150°C. Ethylene glycol, 74.5 grams, was slowly added and the system heated to 175°C. Carbon dioxide, 61 grams, was added over a period of 4 hours. The product was stripped under vacuum (~10 mm Hg) at 190°C, filtered through a 50-50 mixture of Hi - Flo and Celite 512, diatomaceous earth products available from Manville, Filtration and Minerals Division, Denver, CO, to yield 485 grams of a calcium over-based sulfurized alkylphenol having a Total Base Number of 334, a viscosity of 2405 centistokes at 100°C; a sulfur content of 2.7 weight percent; and a calcium content of 12.1 weight percent.

The compositions of this invention as well as prior art compositions were analyzed by the following dialysis and <sup>1</sup>H-NMR technique (Example 18) to determine the content of Group II metal sulfurized alkylphenol as well as unsulfurized Group II metal alkylphenol.

#### Example 18

The compositions of this invention as well as prior art compositions are analyzed in the following manner. The Group II metal overbased sulfurized alkylphenol additive (50 grams) is weighed into an acetone - rinsed dialysis bag (Ramses No. 18 prophylactic bag). The bag is suspended in a 2-liter beaker containing 1.5 liters of 60 volume percent of methyl ethyl ketone (MEK), and 40 volume percent t-butanol. The solution is stirred with a magnetic stirrer at ambient temperature. The solution is changed every 24 hours for seven days. The combined dialyzate solutions are stripped using a rotary evaporator and finally at 1 mm Hg vacuum at 85°C to yield a product which is weighed. This product contains diluent oil (Cit - Con 100N) and unsulfurized alkylphenol starting material as determined by <sup>1</sup>H-NMR in hexamethylphosphoramide (HMPA) solvent. In this solvent the unsulfurized alkylphenol shows peaks in the <sup>1</sup>H-NMR at

10.00 to 10.11 ppm relative to tetramethylsilane (TMS) added as an internal standard. The alkylphenols of Examples 1-4 show this  $^1\text{H-NMR}$  peak and so it is diagnostic for unsulfurized alkylphenol. The solid residue in the dialysis bag is weighed. This residue contains greater than 95 percent of all the calcium (or other Group II metal) in the original Group II metal overbased sulfurized alkylphenol preparations and is referred to as the "actives". This residue or "actives" contains the calcium sulfurized overbased alkylphenol and any unsulfurized calcium alkylphenol. The composition of the "actives" is determined by the following analysis. The "actives" are dissolved in mixed hexanes and then treated with 100 ml of concentrated hydrochloric acid in 100% ethanol. After the hydrochloric acid addition the mixture is stirred for one hour at ambient temperature to effect complete decalcification of the "actives". The liberated sulfurized alkylphenol and in some cases the unsulfurized alkylphenol are obtained by water washing the hexane solution; washing the hexane solution with 10 percent aqueous sodium bicarbonate; and then stripping the hexane solution at 120 mm Hg at 80-85°C to yield the decalcified "actives" product which are analyzed by  $^1\text{H-NMR}$  in hexamethylphosphoramide (HMPA) as solvent containing TMS as internal standard. The unsulfurized alkylphenol shows a peak at 10.00 to 10.11 and is referred to as the  $S_0$  peak. The sulfurized alkylphenols show peaks at 10.40-10.50 for the monosulfide bridged alkylphenols and is referred to as the  $S_1$  peak. The sulfurized alkylphenols also show peaks at 10.90 to 11.00 for the disulfide bridged alkylphenols and is referred to as the  $S_2$  peak. The areas for these peaks are obtained by integration on a Varian T60 or a General Electric QE-300 MHz NMR spectrometer. The integrated areas are converted to mole percents by dividing the  $S_1$  and  $S_2$  integrated peak area by two (assuming dimeric structures).

As used herein and described above, the term "actives" is a measure of the amount of the Group II metal unsulfurized alkylphenol and the Group II metal sulfurized alkylphenol contained in the composition which can be determined by this procedure as well as other standard analytical techniques.

TABLE IV

ANALYSIS OF ACTIVES OBTAINED FROM EXAMPLE 18					
	Mole Percent of actives as			TBN	Viscosity (cst-100°C)
	$S_0^{(1)}$	$S_1^{(2)}$	$S_2^{(3)}$		
Example 11	0	30	70	349	441
Comparative Example B	15	20	65	333	538
Example 12	0	34	66	352	893
Comparative Example C	18	29	53	331	907
Comparative Example E	16	25	59	334	2,405

1.  $S_0$  = mole percent of calcium (unsulfurized alkylphenol)

2.  $S_1$  = mole percent of calcium (monosulfide alkylphenol)

3.  $S_2$  = mole percent of calcium (disulfide alkylphenol)

Table V below establishes that Group II metal unsulfurized alkylphenol content is detrimental to a Group II metal overbased sulfurized alkylphenol composition. In particular, as shown in this table, the calcium salt of the alkylphenol of Example 3 is extremely viscous and accordingly, if present in significant amounts, it will significantly increase the viscosity of the Group II metal overbased sulfurized alkylphenol composition. Likewise, the calcium salt of the alkylphenol of Example 4, while being much less viscous than the calcium salt of the alkylphenol of Example 3, does not contribute much to the Total Base Number of the composition. Accordingly, if present in significant amounts, it will significantly decrease the Total Base Number of the Group II metal overbased sulfurized alkylphenol composition. On the other hand, the Group II metal overbased sulfurized alkylphenols of this invention contain little if any of the unsulfurized Group II metal alkylphenols and accordingly possess a high Total Base Number and an acceptable viscosity. The results of Example 6 are included for illustrative purposes.

TABLE V

	TBN	Viscosity (100°C)
calcium salt of the <sup>(a)</sup> alkylphenol of Ex. 3	211	too viscous to measure
50% dilution with Cit-Con 100N	105	112 centistokes
calcium salt of the <sup>(a)</sup> alkylphenol of Ex. 4 (represents approx. 50% conversion)	54	18 centistokes
Example 11	349	441 centistokes

(a) prepared by reacting the alkylphenol with excess hydrated lime (0.66 eq.) in ethylene glycol at 175°C

Example 19

A formulated oil containing a Group II metal overbased sulfurized alkylphenol of the invention was tested in a Sequence V-D Test method (according to candidate test for ASTM). This procedure utilizes a Ford 2.3-liter, four-cylinder Pinto engine. The test method simulates a type of severe field test service characterized by a combination of low speed, low temperature "stop and go" city driving and moderate turnpike operation. The effectiveness of the additives in the oil is measured in terms of the protection against sludge and varnish deposits on a 0 to 10 scale with 0 being black and 10 indicating no varnish or sludge deposits. The results are indicated in Table VI.

Sequence V-D test was run using a product prepared similarly to that described in Examples 6 and 7. These products were compared to a 250 TBN commercial calcium sulfurized alkylphenol prepared from alkylphenol described in Example 3.

The compositions of the formulated oils were: 5.25% of a bis-polyisobutenyl succinimide; 20 millimoles per kilogram of an overbased hydrocarbyl sulfonate as described in Example 5; 20 millimoles per kilogram of a 320 TBN hydrocarbyl sulfonate, 82 millimoles per kilogram of the product prepared similarly to Examples 6 and 7, 20 millimoles per kilogram of a zinc dithiophosphate; 20% of a commercial viscosity index improver in 150N/600N Exxon base oil - 85% by weight 150N and 15% by weight 600N.

The comparative reference formulation used the same formulation as above with the exception that 82 millimoles per kilogram of a commercial 250 TBN phenate prepared from the alkylphenol described in Example 3 was used instead of the high TBN phenate prepared similarly to Examples 6 and 7.

SEQUENCE V-D RESULTS			
Formulation containing the Phenate of	Deposit		
	AS <sup>(1)</sup>	AV <sup>(2)</sup>	PV <sup>(3)</sup>
Prior Art (run in 1983)	8.3 <sup>4</sup>	7.9 <sup>4</sup>	7.9 <sup>4</sup>
(run in 1984)	8.9	8.0	8.0
(run in 1985)	8.9	7.7	8.0
High TBN Phenate prepared similarly to Examples 6 and 7 <sup>(5)</sup>	9.6	9.0	8.8
(Run in 1985)			

(1) average sludge

(2) average varnish

(3) piston varnish

(4) average of 6 runs

(5) average of 2 runs

**Claims**

1. A process for preparing a lubricating oil additive comprising an oil-soluble hydrolytically stable Group II metal overbased sulfurized alkylphenol characterised as possessing a Total Base Number of at least 300 and a viscosity of not more than 800 centistokes at 100°C and containing less than 10 mole percent (in the actives) of unsulfurized Group II metal alkylphenol, which process comprises the following steps:

(a) reacting, in a lubricating oil, an alkylphenol, sufficient sulfur to convert the alkylphenol to sulfurized alkylphenol, a catalytic amount of a sulfur-containing sulfurization catalyst and a Group II metal oxide, hydroxide or C<sub>1</sub> - C<sub>6</sub> alkoxide, the molar charge of the Group II metal oxide, hydroxide or C<sub>1</sub> - C<sub>6</sub> alkoxide to alkylphenol being greater than 2; and  
(b) carbonating the reaction product of step (a) with CO<sub>2</sub>

2. A process as claimed in Claim 1, wherein the alkyl group of the alkylphenol contains from 25 to 100 mole percent of predominantly straight chain alkyl groups of from 15 to 35 carbon atoms and from 75 to 0 mole percent of polypropenyl groups of from 9 to 18 carbon atoms.

3. A process as claimed in Claim 2, wherein the alkyl group of the alkylphenol contains approximately 50 mole percent of predominantly straight chain alkyl groups of from 15 to 35 carbon atoms and approximately 50 mole percent of polypropenyl groups of from 9 to 18 carbon atoms.

4. A process as claimed in Claim 1, 2 or 3, wherein the Group II metal is calcium.
5. A process as claimed in Claim 1, 2, 3, or 4, wherein the sulfur-containing sulfurization catalyst is 2-mercapto-benzothiazole.
6. A process as claimed in Claim 1, 2, 3 or 4, wherein the sulfur-containing sulfurization catalyst is calcium polysulfide.
7. A process as claimed in any preceding claim, wherein the sulfur-containing sulfurization catalyst is used in conjunction with a demulsifier.
8. A lubricating oil composition comprising an oil of lubricating viscosity and from 0.5 to 40 weight percent of a lubricating oil additive prepared by a process as claimed in any one of Claims 1 to 7.
9. A lubricating oil composition comprising an oil of lubricating viscosity and
  - (a) from 0.5 to 40 weight percent of a lubricating oil additive prepared by a process as claimed in any one of Claims 1 to 7; and
  - (b) from 0.5 to 40 weight percent of an oil-soluble, Group II metal overbased natural or synthetic hydrocarbyl sulfonate.
10. A lubricating oil additive concentrate comprising from 60 to 20 weight percent of an oil of lubricating viscosity and from 40 to 80 weight percent of a lubricating oil additive prepared by a process as claimed in any one of Claims 1 to 7.
11. In the production of an oil-soluble, Group II metal overbased sulfurized alkylphenol by a process having the following steps:
  - (a) reacting, in a lubricating oil, an alkylphenol, sufficient sulfur to convert the alkylphenol to sulfurized alkylphenol and a Group II metal oxide, hydroxide or C<sub>1</sub> - C<sub>6</sub> alkoxide, the molar charge of the Group II metal oxide, hydroxide or C<sub>1</sub> - C<sub>6</sub> alkoxide to alkylphenol being greater than 2; and
  - (b) carbonating the reaction product of step (a) with CO<sub>2</sub>;the use of a catalytic amount of a sulfur-containing sulfurization catalyst in step (a) for the purpose of obtaining a reaction product which has a Total Base Number of at least 300, a viscosity of not more than 800 centistokes at 100°C and less than 10 mole percent (in the actives) of unsulfurized Group II metal alkylphenol.

#### Patentansprüche

1. Verfahren zur Herstellung eines Schmieröl-Additivs, beinhaltend ein öllösliches, hydrolytisch stabiles, überbasisch gemachtes und sulfurisiertes Gruppe-II-Metall-Alkylphenol, das sich auszeichnet durch eine Gesamtbasenzahl von mindestens 300, eine Viskosität bei 100°C von nicht mehr als 800 und einen Gehalt von weniger als 10 Mol.% (bezogen auf den aktiven Teil) an nichtsulfuriertem Gruppe-II-Metall-Alkylphenol, wobei das Verfahren folgende Schritte umfaßt:
  - (a) Umsetzen - in Schmieröl - von Alkylphenol, Schwefel in einer Menge, daß das Alkylphenol in sulfurisiertes Alkylphenol umgesetzt wird, schwefelhaltigem Sulfidierungskatalysator in katalytischer Menge sowie einem Gruppe-II-Metalloxid, -hydroxid oder -C<sub>1</sub>-C<sub>6</sub>-alkoxid, wobei die molare Zugabe an Gruppe-II-Metalloxid, -hydroxid oder -C<sub>1</sub>-C<sub>6</sub>-alkoxid zu Alkylphenol größer ist als 2; und
  - (b) Carbonatisieren des Reaktionsprodukts aus Schritt (a) mit CO<sub>2</sub>.
2. Verfahren nach Anspruch 1, wobei die Alkylgruppe des Alkylphenols 25 bis 100 Mol.% vorwiegend geradkettige Alkylgruppen mit 15 bis 35 Kohlenstoffatomen enthält sowie 75 bis 0 Mol.% Polypropenylgruppen mit 9 bis 18 Kohlenstoffatomen.
3. Verfahren nach Anspruch 2, wobei die Alkylgruppe des Alkylphenols etwa 50 Mol.% vorwiegend geradkettige Alkylgruppen mit 15 bis 35 Kohlenstoffatomen enthält sowie etwa 50 Mol.% Polypropenylgruppen mit 9 bis 18 Kohlenstoffatomen.

4. Verfahren nach Anspruch 1, 2 oder 3, wobei das Metall der II. Gruppe Calcium ist.
5. Verfahren nach Anspruch 1, 2, 3 oder 4, wobei der schwefelhaltige Sulfidierungskatalysator 2-Mercaptobenzotriazol ist.
- 5 6. Verfahren nach Anspruch 1, 2, 3 oder 4, wobei der schwefelhaltige Sulfidierungskatalysator Calciumpolysulfid ist.
7. Verfahren nach einem der vorstehenden Ansprüche, wobei der schwefelhaltige Sulfidierungskatalysator zusammen mit einem Demulgator eingesetzt wird.
- 10 8. Schmieröl-Zusammensetzung, beinhaltend ein Öl mit Schmierviskosität und 0,5 bis 40 Gew.% Schmieröl-Additiv, hergestellt mit einem Verfahren nach einem der Ansprüche 1 bis 7.
9. Schmieröl-Zusammensetzung, beinhaltend ein Öl mit Schmierviskosität und  
15 (a) 0,5 bis 40 Gew.% Schmieröl-Additiv, hergestellt mit einem Verfahren nach einem der Ansprüche 1 bis 7; und  
(b) 0,5 bis 40 Gew.% öllösliches, überbasisch gemachtes, natürliches oder synthetisches Gruppe-II-Metall-Kohlenwasserstoffsulfonat.
- 20 10. Schmieröladditiv-Konzentrat, beinhaltend 60 bis 20 Gew.% Öl mit Schmierviskosität und 40 bis 80 Gew.% Schmieröl-Additiv, hergestellt mit einem Verfahren nach einem der Ansprüche 1 bis 7.
11. Bei der Herstellung eines öllöslichen, hydrolytisch stabilen, überbasisch gemachten und sulfurierten Gruppe-II-Metall-Alkylphenols, in einem Verfahren mit folgenden Schritten: (a) Umsetzen - in Schmieröl - von Alkylphenol, Schwefel in einer Menge, daß das Alkylphenol in sulfuriertes Alkylphenol umgesetzt wird, einem Gruppe-II-Metalloxid, -hydroxid oder -C<sub>1</sub>-C<sub>6</sub>-alk-oxid, wobei die molare Zugabe an Gruppe-II-Metalloxid, -hydroxid oder -C<sub>1</sub>-C<sub>6</sub>-Alkoxid zu Alkylphenol größer ist als 2; und (b) Carbonatisieren des Reaktionsprodukts aus Schritt (a) mit CO<sub>2</sub>; die Verwendung einer katalytischen Menge schwefelhaltigen Sulfidierungskatalysator in Schritt (a), damit man ein Reaktionsprodukt erhält, das eine Gesamtbasenzahl von mindestens 300 hat, eine Viskosität bei 100°C von nicht mehr als 800 Centistokes und einen Gehalt von weniger als 10 Mol.% (bezogen auf den aktiven Teil) an nichtsulfuriertem Gruppe-II-Metall-Alkylphenol.

#### Revendications

- 35 1. Procédé de production d'un additif pour huile lubrifiante, comprenant un alkylphénol sulfuré rendu surbasique par un métal du Groupe II, stable à l'hydrolyse et soluble dans l'huile, caractérisé comme possédant un Indice de Basicité Totale d'au moins 300 et une viscosité à 100°C ne dépassant pas 800 centistokes et contenant moins de 10 moles % (sur bases actives) d'alkylphénol non sulfuré de métal du Groupe II, ce procédé comprenant les étapes qui consistent :  
40 (a) à faire réagir, dans une huile lubrifiante, un alkylphénol, une quantité suffisante de soufre pour convertir l'alkylphénol en alkylphénol sulfuré, une quantité catalytique d'un catalyseur de sulfuration contenant du soufre et un oxyde, hydroxyde ou alcoolate en C<sub>1</sub> à C<sub>6</sub> d'un métal du Groupe II, le rapport molaire de l'oxyde, hydroxyde ou alcoolate en C<sub>1</sub> à C<sub>6</sub> de métal du Groupe II à l'alkylphénol étant supérieur à 2; et  
45 (b) à carbonater le produit de réaction de l'étape (a) avec du CO<sub>2</sub>.
2. Procédé suivant la revendication 1, dans lequel le groupe alkyle de l'alkylphénol contient 25 à 100 moles % de groupes alkyle principalement à chaîne droite ayant 15 à 35 atomes de carbone, et 75 à 0 moles % de groupes polypropényle ayant 9 à 18 atomes de carbone.
- 50 3. Procédé suivant la revendication 2, dans lequel le groupe alkyle de l'alkylphénol contient environ 50 moles % de groupes alkyle principalement à chaîne droite ayant 15 à 35 atomes de carbone et environ 50 moles % de groupes polypropényle ayant 9 à 18 atomes de carbone.
- 55 4. Procédé suivant la revendication 1, 2 ou 3, dans lequel le métal du Groupe II est le calcium.
5. Procédé suivant la revendication 1, 2, 3 ou 4, dans lequel le catalyseur de sulfuration contenant du soufre est le

2-mercapto-benzothiazole.

6. Procédé suivant la revendication 1, 2, 3 ou 4, dans lequel le catalyseur de sulfuration contenant du soufre est un polysulfure de calcium.
7. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le catalyseur de sulfuration contenant du soufre est utilisé conjointement avec un désémulsionnant.
8. Composition d'huile lubrifiante comprenant une huile de viscosité propre à la lubrification et 0,5 à 40 % en poids d'un additif pour huile lubrifiante préparé par un procédé tel que revendiqué dans l'une quelconque des revendications 1 à 7.
9. Composition d'huile lubrifiante, comprenant une huile de viscosité propre à la lubrification et
  - (a) 0,5 à 40 % en poids d'un additif pour huile lubrifiante préparé par un procédé tel que revendiqué dans l'une quelconque des revendications 1 à 7 ; et
  - (b) 0,5 à 40 % en poids d'un hydrocarbyle-sulfonate naturel ou synthétique soluble dans l'huile rendu surbasique par un métal du Groupe II.
10. Concentré d'additif pour huile lubrifiante, comprenant 60 à 20 % en poids d'une huile de viscosité propre à la lubrification et 40 à 80 % en poids d'un additif pour huile lubrifiante préparé par un procédé tel que revendiqué dans l'une quelconque des revendications 1 à 7.
11. Dans la production d'un alkylphénol sulfuré rendu surbasique par un métal du Groupe II, soluble dans l'huile, par un procédé ayant les étapes suivantes :
  - (a) réaction, dans une huile lubrifiante, d'un alkylphénol, d'une quantité suffisante de soufre pour convertir l'alkylphénol en alkylphénol sulfuré et un oxyde, hydroxyde ou alcoolate en C<sub>1</sub> à C<sub>6</sub> de métal du Groupe II, le rapport molaire de l'oxyde, hydroxyde ou alcoolate en C<sub>1</sub> à C<sub>6</sub> de métal du Groupe II à l'alkylphénol étant supérieur à 2 ; et
  - (b) carbonatation avec du CO<sub>2</sub> du produit de réaction de l'étape (a) ;

l'utilisation d'une quantité catalytique d'un catalyseur de sulfuration contenant du soufre dans l'étape (a) en vue d'obtenir un produit de réaction qui a un Indice de Basicité Totale d'au moins 300, une viscosité à 100°C ne dépassant pas 800 centistokes et une teneur de moins de 10 moles % (sur bases actives) en alkylphénol non sulfuré de métal du Groupe II.